EXPLORING OLD AND NEW BENZENE FORMATION PATHWAYS IN LOW-PRESSURE PREMIXED FLAMES OF ALIPHATIC FUELS

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A modeling study of benzene and phenyl radical formation was performed for three low-pressure premixed laminar flat flames having an unsaturated C_2 or C_3 hydrocarbon fuel (acetylene, ethylene, and propene). Predictions using three published detailed elementary-step chemical kinetics mechanisms were tested against molecular beam mass spectrometry (MBMS) species profile data for all three flames. The differences between the predictive capabilities of the three mechanisms were explored, with an emphasis on benzene formation pathways. A new chemical kinetics mechanism was created combining features of all three published mechanisms. Included in the mechanism were several novel benzene formation reactions involving combinations of radicals such as $C_2H + C_4H_5$, $C_2H_3 + C_4H_3$, and $C_5H_3 + CH_3$. Reactions forming fulvene (a benzene isomer) were included, such as C_3H_3(propargyl) $+$ C_3H_5(allyl), as well as fulvene to benzene reactions.

Predictions using the new mechanism showed virtually all of the benzene and phenyl radical to be formed by reactions of either $C_3H_3 + C_3H_3$ or $C_3H_3 + C_3H_5$, with the relative importance being strongly dependent on the fuel. $C_5H_3 + CH_3$ played a minor role in fulvene formation in the acetylene flame. The $C_2H_x + C_4H_x$ reactions did not contribute noticeably to benzene or phenyl radical formation in these flames, sometimes being a major decomposition channel for either fulvene or phenyl radical. The formation pathways for C_3H_3 and C_3H_5 were delineated for the three flames; although the key reactions differed from flame to flame, $^1CH_2 + C_2H_2 \Leftrightarrow C_3H_3 + H$ was important for all three flames.

Introduction

A molecular-level understanding of combustion chemistry is essential for controlling the products of molecular-weight growth, which can lead to the formation of polycyclic aromatic hydrocarbons (PAHs), many of which are known mutagens and/or carcinogens. The PAHs themselves are likely precursors of soot particles in flames. For flames of aliphatic fuels, all of the aromatic rings, including the first, need to be formed by combination of smaller hydrocarbon fragments, thus providing motivation for understanding benzene formation in combustion.

Considering the level of interest in benzene formation, the lack of consensus on what the major reaction pathways are might be surprising to the casual observer. Thorough reviews of all but the most recent work have been provided by Westmoreland et al. [1] and Melius et al. [2]. Two broad types of ring-forming reactions appear: (1) acetylene (C_2H_2) addition to a C_4 vinyl radical, with subsequent cyclization, that is, reactions R1 [3] and R2 [4] in Table 1 and (2) combination of resonantly stabilized free radicals (RSFRs), with subsequent rearrangement and ring formation, for example, reaction R3a, propargyl (H_2CCCH) radical recombination, $2C_3H_3 \Leftrightarrow C_6H_5$(phenyl) $+$ H [2,5,6].

In the acetylene-addition reactions, one reactant (C_2H_2) is a major product of fuel-rich combustion, present in high concentrations, and the adduct does not require intramolecular rearrangements prior to cyclization. However, both n-C_4H_3 (HCCHCCH) and n-C_4H_5 (CH$_2$CHCHCH) have more stable isomers—i-C_4H_3 (H$_2$CCCCH) and i-C_4H_5 (CH$_2$CHCCH$_2$)—into which they can readily be converted [5], greatly diminishing the amount of the n-C_4H_3 and n-C_4H_5 available. While R1 and R2 are strongly exothermic, they also have large decreases in entropy, becoming less favored at higher temperatures. Furthermore, R2 has a net decrease in number of moles, causing it to be less favored at lower pressures.

Relatively high concentrations of C_3H_3 were also seen in flames, due to the resonance-enhanced stability of propargyl. In low-pressure acetylene [1], 1,3-butadiene (C_4H_6) [4], and benzene [7] flames, peak mole fractions of C_3H_3 near 10^{-3} were observed. Recombination of propargyl radical also has no barrier to forming a ring-containing C_6 species, whether it be fulvene, benzene, or phenyl $+$ H [2,5,6]; R3 can therefore become a direct aromatic ring formation route, especially at low pressures. However, reaction R3a has a crossover temperature (above which $\varDelta G > 0$) of 1729 K, and is much less

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TABLE 1
Rate coefficients for reactions which are discussed in the text and in subsequent figures, and which are used in the expanded mechanism called M1a later in the text

Number	Reaction	A	b	E	Reference
R1	$C_2H_2 + n\text{-}C_4H_5 \Leftrightarrow C_6H_6 + H$	8.209×10^3	0.801	6348.	[26], pw
R2	$n\text{-}C_4H_3 + C_2H_2 \Leftrightarrow C_6H_5$	1.667×10^{10}	0.446	7719.3	[26], pw
R3a	$2\ C_3H_3 \Leftrightarrow C_6H_5 + H$	5.00×10^{12}	0	0	pw
R3b	$2\ C_3H_3 \Leftrightarrow$ fulvene	4.50×10^{12}	0	0	pw
R3c	$2\ C_3H_3 \Leftrightarrow n\text{-}C_5H_3 + CH_3$	5.00×10^{11}	0	0	pw
R4	$C_3H_3 + C_3H_5 \Leftrightarrow$ fulvene $+ H + H$	5.562×10^{20}	-2.535	1692.	[9]
R5a	$i\text{-}C_5H_3 + CH_3 \Leftrightarrow$ fulvene	1.40×10^{13}	0	0	[11], pw
R5b	$i\text{-}C_5H_3 + CH_3 \Leftrightarrow C_6H_5 + H$	6.00×10^{12}	0	0	[11], pw
R6a	$n\text{-}C_5H_3 + CH_3 \Leftrightarrow$ fulvene	1.00×10^{13}	0	0	[11], pw
R6b	$n\text{-}C_5H_3 + CH_3 \Leftrightarrow C_6H_5 + H$	1.00×10^{13}	0	0	[11], pw
R7	$^1CH_2 + C_2H_2 \Leftrightarrow C_3H_3 + H$	1.80×10^{14}	0	0	[5,21]
R8a	$C_2H_3 + CH_3 \Leftrightarrow C_3H_6$	3.688×10^{30}	-5.034	7691.9	[31]
R8b	$C_2H_3 + CH_3 \Leftrightarrow C_3H_5 + H$	2.861×10^{21}	-2.118	11841.8	[31]
R9a	$n\text{-}C_4H_3 + C_2H_3 \Leftrightarrow$ fulvene	4.00×10^{12}	0	0	pw
R9b	$n\text{-}C_4H_3 + C_2H_3 \Leftrightarrow C_6H_5 + H$	1.60×10^{13}	0	0	pw
R10a	$n\text{-}C_4H_5 + C_2H \Leftrightarrow$ fulvene	4.00×10^{12}	0	0	pw
R10b	$n\text{-}C_4H_5 + C_2H \Leftrightarrow C_6H_5 + H$	1.60×10^{13}	0	0	pw
R11a	$i\text{-}C_4H_3 + C_2H_3 \Leftrightarrow$ fulvene	1.00×10^{13}	0	0	pw
R11b	$i\text{-}C_4H_3 + C_2H_3 \Leftrightarrow C_6H_5 + H$	6.00×10^{12}	0	0	pw
R11c	$i\text{-}C_4H_3 + C_2H_3 \Leftrightarrow 2C_3H_3$	4.00×10^{12}	0	0	pw
R12a	$i\text{-}C_4H_5 + C_2H \Leftrightarrow$ fulvene	1.00×10^{13}	0	0	pw
R12b	$i\text{-}C_4H_5 + C_2H \Leftrightarrow C_6H_5 + H$	6.00×10^{12}	0	0	pw
R12c	$i\text{-}C_4H_5 + C_2H \Leftrightarrow 2C_3H_3$	4.00×10^{12}	0	0	pw

Units are cm^3, mol, s, kcal. pw = present work.

thermodynamically favored than R1, with a cross-over temperature of 2218 K.

Other pathways to benzene have been proposed. Lindstedt and Skevis [8] considered $C_2H_3 + C_4H_4(CH_2CHCCH) \Leftrightarrow C_6H_6(benzene) + H$ and $C_2H_3 + C_4H_6(CH_2CHCHCH_2) \Leftrightarrow C_6H_8(1,4\text{-}cyclohexadiene) + H$, with the C_6H_8 decomposing to benzene and H_2. Marinov et al. [9] proposed a combination of two C_3 RSFRs, propargyl and allyl (R4). Moskaleva et al. [10] considered methyl + cyclopentadienyl (also a RSFR), forming methylcyclopentadiene, which forms fulvene, then benzene. Mebel et al. [11] calculated the potential energy surface of $C_6H_6(benzene) \Leftrightarrow C_5H_3 + CH_3$ reactions. The reverse reactions can also be possible benzene formation pathways (R5, R6) from either of the two most stable forms of C_5H_3, $H_2CCCCCH$ (here called $i\text{-}C_5H_3$) and $HCCCHCCH$ ($n\text{-}C_5H_3$). Walch [12] calculated the potential energy surface of both R2 and the reaction of $i\text{-}C_4H_3$ with acetylene.

There are not infinitely many benzene formation reactions. Considering only bimolecular reactions, the two reactants should collectively contain precisely six carbon atoms and roughly six hydrogen atoms (for the above examples, five to nine hydrogen atoms). An ultimate goal would be to determine which of the conceivable benzene formation pathways are important. The answer would be complex, probably depending on the fuel and on the reactor conditions, even for the rather restricted case of low-pressure premixed flames of aliphatic fuels.

Approach

To assess the possible importance of various benzene formation pathways, we performed a modeling study on three sets of flame data. The flames selected were all fuel-rich low-pressure premixed laminar flat flames with feeds containing an unsaturated C_2 or C_3 hydrocarbon as a fuel, oxygen, and argon; all three flames had species concentration profiles (including benzene) measured by molecular beam mass spectrometry (MBMS), as well as experimental temperature profiles. The three flames were (F1) a 20 Torr C_2H_2 flame with 45 mol % Ar, cold gas velocity of 97 cm/s, and an equivalence ratio (ϕ) of 2.5 [13]; (F2) a 20 Torr C_2H_4 flame, 50 mol % Ar, 62.5 cm/s, $\phi = 1.9$ [14]; (F3) a 37.5 Torr C_3H_6 (propene) flame, 25 mol % Ar, 48.2 cm/s, $\phi = 2.32$ [15]. Modeling calculations employed the CHEMKIN pro-

grams [16–20]. Full multicomponent diffusion, including thermal diffusion, was calculated. The catalytic boundary condition for H-atom recombination at the burner surface was also included. Experimental temperature profiles were used as input, in lieu of solving the energy equation.

Three different chemical kinetics mechanisms were tested. The first (M1) was the mechanism of Pauwels et al. [21], derived from Miller and Melius [5], plus 47 reactions describing the chemistry of propene and of the three C_3H_5 isomers, from Marinov et al. [22,23], which allowed modeling of the propene flame (F3). The second mechanism (M2) was from Richter et al. [24], based on Zhang and McKinnon [25], with extensive PAH formation chemistry at low pressure (20 Torr). To afford a more complete comparison, the reaction $^1CH_2 + C_2H_2 \Leftrightarrow C_3H_3 + H$ (R7) was added to M2. The third mechanism (M3) was from Marinov et al. [9,22,23]. M3 built on the Miller and Melius [5] chemistry by including additional reactions of RSFRs and PAH formation reactions at atmospheric pressure. While many other chemical kinetics mechanisms are available in the literature, the three chosen here provided a reasonable basis for comparison, showing areas in which M1 can be improved.

Modeling Results

All three mechanisms did well at predicting the decay of fuel and O_2 in the three flames. Table 2 lists the experimental and the predicted peak mole fractions for the three flames, as well as the peak locations (in centimeter height above burner). The predictions also included those from an extensively modified and expanded version of M1, called M1a. The key changes made in forming M1a, and the modeling results using M1a, are discussed below.

All three mechanisms predicted both the peak concentration and the shape of the C_2H_2 profiles quite well in all three flames. M3 overpredicted peak C_6H_6 mole fractions for all three flames. Many of the pressure-dependent reactions in M3 had rate coefficients that are fit for atmospheric pressure, so M3 overpredicted molecular-weight growth in such reactions as $C_2H_3 + CH_3 \Leftrightarrow C_3H_6$ (R8a), hence the overprediction of C_4H_3 and C_4H_5 in all three flames. However, C_6H_5 concentrations were underpredicted.

Peak C_6H_6 mole fraction predictions from M2 were within 25% for F1, a factor of 10 low for F2, and roughly 100 times too low for F3. M2 did not include the propargyl recombination reaction (R3), which most likely explains the C_6H_6 shortfall and C_3H_3 overprediction for the three flames. In F1, formation of C_6H_6 was by $C_3H_3 + C_3H_4$(allene) $\Leftrightarrow C_6H_6 + H$, yet C_3H_4 was also overpredicted.

The peak predicted C_6H_6 mole fractions from M2 were 74% of the peak measured value for F1, 11% for F2, and 0.89% for F3. M2 does not include the propargyl recombination reaction (R3), which most likely explains the C_6H_6 shortfall and C_3H_3 over-prediction for the three flames. In F1, formation of C_6H_6 was by $C_3H_3 + C_3H_4$ (allene) $\Leftrightarrow C_6H_6 + H$, yet C_3H_4 was also overpredicted.

The predicted peak C_6H_6 mole fractions using M1 ranges from 30% to 50% of the data. Peak C_3H_3 mole fractions were overpredicted for all three flames, although for F1 and F2 the M1 predictions came closest to the data. Peak C_4H_3 mole fractions were higher than the data for all three flames. Predicted C_4H_5 peaks were 3.3% of the measured peak for F1, 830% for F2, and 84% for F3, C_6H_5 predictions were 12% of the measured peak for F2 and 140% for F3, following the same trend as the M2 predictions.

Expanded Benzene Formation Chemistry

Building on the mechanism M1 [5,21], a significantly expanded mechanism (M1a) was created, containing 91 species and 527 reactions. (Note: The mechanism is available by contacting the authors at cjpope@sandia.gov or jamille@ca.sandia.gov.) Beyond the C_3H_5 and C_3H_6 species and reactions, two other large additions were made using reactions from either M2 [24] or M3 [22,23]. Enhanced benzene oxidation chemistry led to inclusion of five C_5 species (C_5H_5O, C_5H_6, linear C_5H_5, C_5H_4O, and C_5H_4OH). Molecular-weight growth chemistry up to $C_{10}H_8$ (naphthalene) was added; although many of these reactions were contained in both M2 and M3, rates from M2 had been fitted for low pressures.

In addition to the sweeping changes mentioned above, several individual reactions were added, and several key rate coefficients were modified. Rate coefficients for reactions R1 and R2 were from Wang and Frenklach [26]. As an upper bound for these rates, the 20 Torr fits for all four product channels [26] were summed and used as the rate for R2. Similarly, the sum of the four product channels for $C_2H_2 + n = C_4H_5$ for 0–90 Torr [26] was used for the R1 rate coefficient. The resulting sums were fit into the three-parameter Arrhenius form. The barrier height used [26] for R2 was 3.1 kcal/mol; the barrier calculated by Walch [12] was 8.3 kcal/mol, close to the AM1 barrier height [26]. Accordingly, the activation energy for R2 was increased by 5.2 kcal/mol, as was the fitted activation energy for R1. The rate for $C_6H_5 + C_2H_2 \Leftrightarrow C_6H_5C_2H + H$ was taken from Yu et al. [27] by fitting the sum of the rates for all product channels.

The overall rate for $C_2H_3 + C_2H_3$ was changed to 9.0×10^{13} cm^3/mol s [28,29]. Consistent with the

TABLE 2
Experimental peak mole fractions for selected species, with predicted values from mechanisms, M1, M1a, M2, M3:
(a) flame F1, (b) flame F2, (c) flame F3

(a) C_2H_2 flame—F1

Species	M1	M1a	M2	M3	Data
C_2H_2	(0.55)	(0.57)	(0.60)	(0.58)	(0.56)
C_2H_3	4.78E-05(0.70)	4.66E-05(0.80)	1.74E-05(0.73)	6.66E-05(0.75)	3.77E-05(0.58)
C_3H_3	5.63E-04(0.72)	5.28E-04(0.72)	1.29E-02(0.82)	1.89E-03(0.72)	2.24E-04(0.80)
C_3H_5	1.27E-05(0.69)	7.21E-06(0.59)	1.70E-04(0.56)	4.34E-05(0.71)	xxx
C_4H_3	9.45E-05(0.80)	9.20E-05(0.80)	3.51E-04(0.88)	1.02E-04(0.82)	8.76E-06(0.59)
C_4H_5	1.04E-06(0.80)	5.77E-06(0.78)	1.60E-06(0.69)	6.94E-05(0.82)	3.13E-05(0.79)
C_6H_5	2.24E-06(0.60)	2.71E-06(0.62)	5.23E-07(0.80)	1.44E-05(0.69)	xxx
C_6H_6	2.31E-05(0.55)	4.99E-05(0.65)	4.35E-05(0.59)	7.27E-04(0.60)	5.87E-05(0.60)

(b) C_2H_4 flame—F2

Species	M1	M1a	M2	M3	xData
C_2H_2	2.91E-02(0.95)	3.03E-02(1.00)	2.56E-02(0.75)	3.68E-02(0.95)	3.33E-02(0.90)
C_2H_3	1.08E-03(0.80)	9.05E-04(0.85)	4.55E-04(0.62)	3.85E-04(0.70)	6.74E-05(0.67)
C_3H_3	6.77E-04(0.90)	4.58E-04(0.90)	2.82E-03(0.90)	1.01E-03(1.00)	4.26E-04(1.03)
C_3H_5	6.00E-04(0.70)	2.88E-04(0.75)	2.16E-05(0.50)	6.57E-04(0.65)	6.80E-05(0.78)
C_4H_3	1.23E-04(0.98)	1.36E-04(1.12)	6.84E-05(0.90)	9.85E-05(0.95)	6.70E-06(0.71)
C_4H_5	2.42E-05(0.62)	8.93E-05(0.70)	2.79E-05(0.55)	3.18E-04(0.70)	2.90E-06(0.58)
C_6H_5	2.08E-06(0.72)	1.96E-06(0.80)	3.92E-07(0.06)	1.62E-06(0.75)	1.70E-05(0.81)
C_6H_6	9.84E-06(0.70)	1.90E-05(0.45)	3.54E-06(0.45)	1.18E-04(0.65)	3.33E-05(0.93)

(c) C_3H_6 flame—F3

Species	M1	M1a	M2	M3	Data
C_2H_2	3.29E-02(0.45)	5.08E-02(0.45)	5.22E-02(0.56)	5.79E-02(0.39)	3.69E-02(0.43)
C_2H_3	6.70E-04(0.35)	1.10E-03(0.38)	2.45E-04(0.44)	3.01E-04(0.35)	2.48E-03(0.34)
C_3H_3	3.95E-03(0.38)	1.83E-03(0.38)	7.77E-03(0.47)	2.88E-03(0.41)	3.09E-03(0.34)
C_3H_5	1.09E-02(0.31)	6.07E-03(0.28)	3.63E-03(0.22)	1.02E-02(0.32)	3.50E-03(0.29)
C_4H_3	6.54E-04(0.45)	7.40E-04(0.40)	2.78E-04(0.48)	3.70E-04(0.45)	1.55E-04(0.43)
C_4H_5	1.01E-04(0.35)	6.12E-04(0.29)	1.04E-06(0.42)	1.56E-03(0.39)	1.20E-04(0.34)
C_6H_5	1.06E-04(0.35)	4.03E-05(0.35)	1.31E-07(0.41)	2.86E-05(0.38)	7.43E-05(0.29)
C_6H_6	6.23E-04(0.32)	1.38E-03(0.25)	1.08E-05(0.19)	3.22E-03(0.31)	1.22E-03(0.39)

Note: Numbers in parentheses give the peak location in cm height above burner. Modeling results for many species are sums of predicted concentrations of more than one isomer. "xxx" means that no data were reported for that species. For F1, C_2H_2 is the fuel; the only values reported are the heights above burner at which the mole fraction is half of its inlet value.

observation of a C_3H_3 + CH_3 product channel [30], the branching ratio was set to 10% i-C_4H_5 + H, 20% C_3H_3 + CH_3, 70% C_2H_2 + C_2H_4. Rates for R8 were from Tsang and Hampson's [31] 20 Torr results. C_3H chemistry was added, with thermochemical properties from Guadagnini et al. [32]. Allyl/propargyl recombination (R4) in M3 formed much of the benzene in F2 and F3, so this reaction was added, although the authors [9] stated the rate coefficient was an upper bound at 1 atm. Also added were two reactions for converting fulvene into benzene. (See Table 1 for rate coefficients of key reactions.)

Radical-Radical Recombination Reactions for C_6H_6 Formation

Several chemically activated radical-radical combinations were proposed as possible benzene-forming reactions in M1a (R5, R6, R9–R12). For propargyl-propargyl recombination, not only the initial adduct but also several of the rearrangement products/intermediates are aliphatic C_6H_6 species [2,5,6]; many other radical-radical combinations can lead to the same aliphatic C_6H_6 species. Both n-C_4H_3 + C_2H_3 and n-C_4H_5 + C_2H can combine to form $CH_2CHCHCHCCH$. $CH_3CHCCHCCH$,

TABLE 3
Standard heats of formation (in kcal/mol) of C_6H_6
species and selected combinations of molecules with
combined empirical formula of C_6H_6

Molecule(s)	ΔH_f° (298 K)
n-C_4H_5 + C_2H	218.7
i-C_4H_5 + C_2H	206.3
o-benzyne + 2H	205.8
n-C_4H_3 + C_2H_3	201.0
i-C_4H_3 + C_2H_3	182.3
C_3H_3 + C_3H_3	172.0 [33,34]
n-C_5H_3 + CH_3	169.9
i-C_5H_3 + CH_3	163.1
C_5H_2 + CH_4	147.3
phenyl + H	131.5
C_4H_2 + C_2H_4	123.8
C_4H_4 + C_2H_2	123.3
$HCCCH_2CHCCH_2$	104.3
$CH_3CHCCHCCH$	99.7
$CH_2CCHCHCCH_2$	96.5
$CH_3CHCCCCH_2$	93.2 [11]
$CH_2CCCHCHCH_2$	85.6 [11]
$CH_2C(CCH)CHCH_2$	82.4
$CH_2CHCHCHCCH$	80.0
Fulvene	52.5
Benzene	19.8

Thermodynamic properties are from Miller and Melius [5] and Kee et al. [20] unless otherwise noted.

formed by n-C_5H_3 + CH_3, which can undergo a hydrogen shift to form $CH_2CHCHCHCCH$. Combination of i-C_4H_3 + C_2H_3 or i-C_4H_5 + C_2H can form $CH_2C(CCH)CHCH_2$. i-C_4H_5 + C_2H can also form CH_2CCHCH_2CCH, as can C_3H_3 + C_3H_3. $CH_3CHCCCCH_2$ from i-C_5H_3 + CH_3 can undergo a hydrogen shift to form $CH_2CCCHCHCH_2$. $CH_2CCCHCHCH_2$ is also a product of i-C_4H_3 + C_2H_3, converting via a hydrogen shift to $CH_2CCHCHCCH_2$, another direct propargyl-propargyl recombination product. Once any of these aliphatic C_6H_6 adducts is formed, the chemistry leading to either fulvene, benzene, or phenyl + H is as described by Miller and coworkers [2,5,6]. The overall rate for adduct formation and subsequent reaction for each of these new reactions was estimated to be 2×10^{13} cm^3/mol s. H-abstraction reactions from these pairs of radicals are also included in the new mechanism, as are reactions interrelating C_5H_2, i-C_5H_3, and n-C_5H_3.

All these new reactions were written in the exothermic direction. Standard heats of formation for the above C_6H_6 species and combinations of molecules with combined empirical formula of C_6H_6 are given in Table 3. The heat of formation used for propargyl radical is 86.0 kcal/mol [33,34], and the

standard entropy is 59.9 cal/mol K [34]; the earlier values used were 83.0 kcal/mol and 61.4 cal/mol K. The less stable propargyl radical results in slightly lower predicted C_3H_3 mole fractions, and therefore a slightly diminished role of C_3H_3 + C_3H_3 in benzene formation. Predicted peak mole fractions of C_4H_3 and C_4H_5 also increased by at least a factor of 3 in all three flames. The total rate used for R3 was 1×10^{13} cm^3/mol s; measured values were 2.4–7.2 $\times 10^{13}$ cm^3/mol s [35–38]. Preliminary master equation calculations [39] showed that at conditions of the flames considered here, very little benzene was formed directly. Accordingly, the branching ratio used had the products being split nearly evenly between fulvene and phenyl + H, with i-C_5H_3 + CH_3 being a minor pathway since it is slightly exothermic. (Not enough confidence was placed in the 2.1 kcal/mol exothermicity of the n-C_5H_3 + CH_3 product channel to believe that it would be significant.)

Discussion of Results from Improved Mechanism

Predictions using M1 and M1a are compared against data in Fig. 1 for C_6H_6. Benzene is the only C_6H_6 species in M1; M1a also includes fulvene. For F1 (Fig. 1a), M1a greatly improves C_6H_6 predictions. Little fulvene is predicted. An improvement is also seen for F2 (Fig. 1b), with an appreciable amount of fulvene predicted early in the flame. M1a slightly overpredicts C_6H_6 concentrations in F3 (Fig. 1c), with fulvene being important early in the flame.

The major reaction pathways leading to phenyl, fulvene, and benzene are shown in Fig. 2. For all three flames, R3 plays a major role. R4 contributes a moderate amount in F2 and F3; in F1, it is a major fulvene decomposition pathway. Use of the 1 atm rate coefficient for this reaction is most likely responsible for the overprediction of C_6H_6 in F3. R1 is almost entirely a phenyl decomposition pathway in F2 and F3; in F1 the reaction is of negligible importance. R2 has no discernible effect for any of the flames studied.

Of the new radical-radical reactions added, only R5a appears as a substantial ring-forming reaction, and then only in F1. The relation of the C_5H_2 and C_5H_3 species with the polyacetylene pool leads to more of these species being formed in F1. Unfortunately, there are no data for testing predicted concentrations of the C_5H_2 and C_5H_3 species. For F2 and F3, the major role of R5 is as a pathway for converting fulvene to benzene. Whether this actually happens is questionable; however, further investigation of the possible role of these C_5H_3 species is indicated. The only other new reactions appearing in Fig. 2 involve i-C_4H_3 + C_2H_3 (R11) as decomposition products of either fulvene or phenyl + H.

No C_2 + C_4 reaction in the mechanism was predicted to lead to benzene formation in any of these
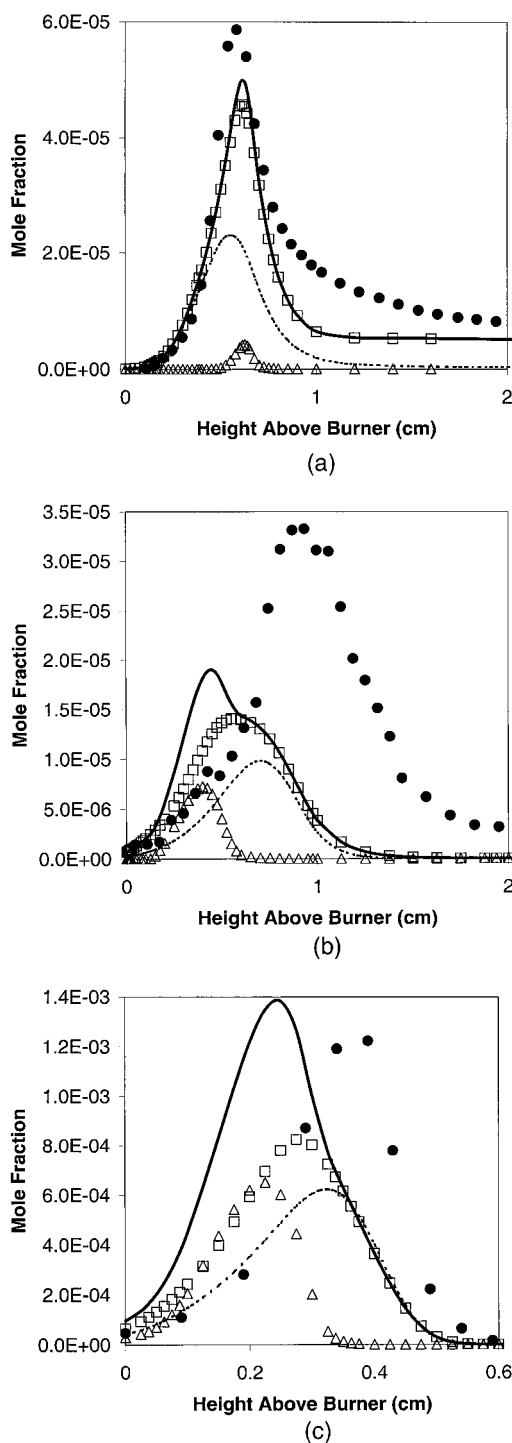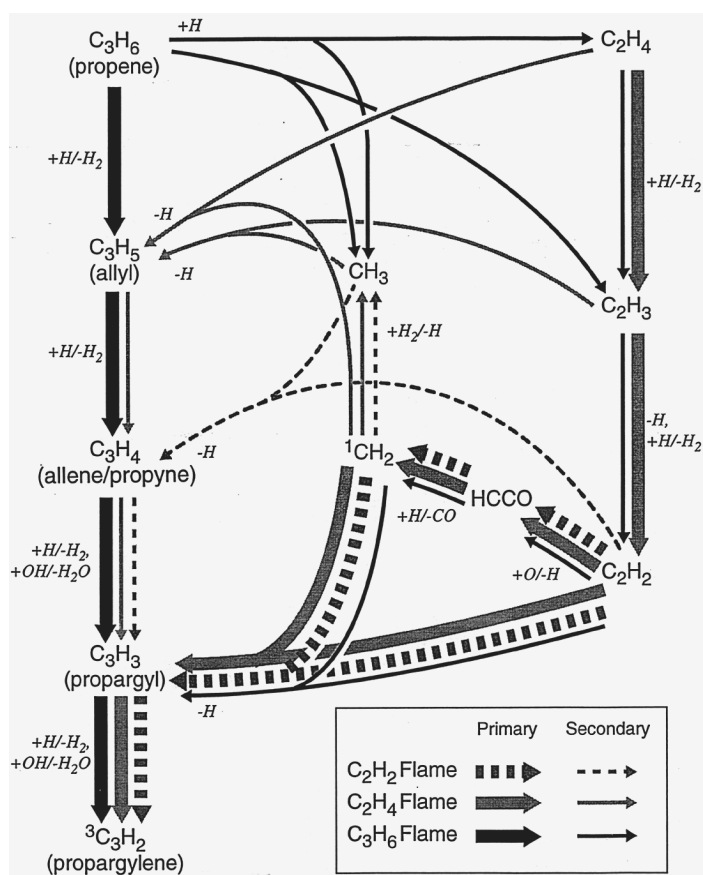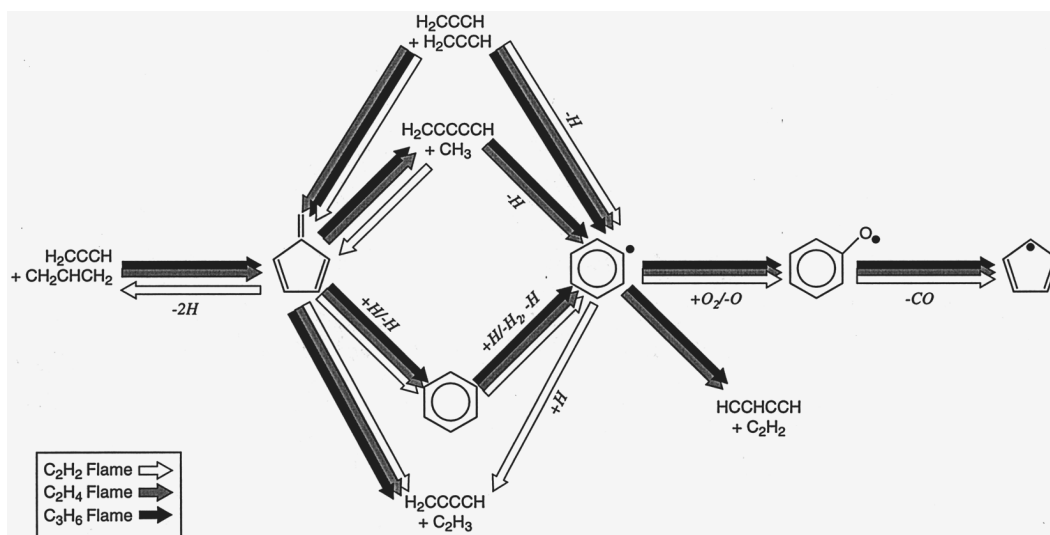
FIG. 1. Predictions of C_6H_6 species from mechanisms M1 and M1a compared with data: (a) C_2H_2 flame (F1), (b) C_2H_4 flame (F2), (c) C_3H_6 flame (F3). Circles, data; dashed line, benzene from M1; open squares, benzene from M1a; open triangles, fulvene from M1a; solid line, total C_6H_6 from M1a.

flames—only reactions involving C_3 radicals led to ring formation. Fig. 3 shows the major predicted pathways for C_3 radical formation from the fuel for the three flames. For F3, the main source of C_3H_3 and C_3H_5 radicals is by successive H abstractions from the fuel. While R7 is the dominant source of C_3 radicals in F1 and F2, it is a secondary pathway in F3, with the fuel decomposing to ethylene or vinyl radical, forming acetylene by H abstraction. In F2, C_2H_4 and C_2H_3 combine with C_1 radicals to form allyl. In F1, the fuel combines with methyl radical to give propyne + H, with the propyne then forming propargyl.

Therefore, for the low-pressure flames studied here, only combinations of C_3 radicals led to production of benzene or phenyl. However, it is conceivable that there would be fuels or flame conditions that would favor the C_2 + C_4 pathways. For example, R2 is the only important molecular-weight growth reaction involving phenyl having a net mole change. The rates of bimolecular reactions, expressed as mol C_6H_5/g gas/s (the molar rate divided by the gas density), would increase linearly with pressure, while those of unimolecular rates would remain constant, all else being equal. The relative importance of R2 to the other molecular-weight growth reactions at higher pressures can then be approximated by looking only at its forward rate, which is 2.4% of the peak of the sum of the net rates of all the other molecular-weight growth reactions for F1, and less than 1% for F2 and F3. Therefore, increased pressure alone would decrease the role of R2 as a phenyl decomposition channel but would not in itself make R2 a major phenyl-producing reaction. This is more noteworthy since C_4H_3 was overpredicted in all three flames, and since the n = C_4H_3/i = C_4H_3 and n-C_4H_5/i-C_4H_5 ratios are at least an order of magnitude above partial equilibrium for all positions in all three flames. Secondary effects of pressure, such as increasing the rates of C_4-radical forming reactions, cannot be ruled out.

In summary, for the three flames considered, the only major formation pathways for benzene or phenyl were the result of combination of C_3 radicals. The C_2H_2 + C_4 radical pathways (R1, R2) did not appear to contribute significantly to single-ring aromatic formation. The relative importance of different benzene/phenyl/fulvene reaction pathways was fuel dependent, as were the major pathways for formation of the C_3 radicals. No claims to generality can be made for other fuels, flow systems, or pressures. However, in modeling of low-pressure C_2H_2 flames [40] and atmospheric-pressure C_2H_4 flames [40–42], recombination of propargyl radical was found to be an important contributor to benzene formation.

The new pathways proposed to C_6H_6 are pertinent to the overall role of RSFRs in benzene formation, since the aliphatic C_6H_6 adducts formed are the

FIG. 2. Predicted major reaction pathways involving phenyl, benzene, and fulvene for the three flames from mechanism M1a. See text for discussion.

FIG. 3. Predicted primary and secondary formation pathways of C_3 radicals for the three flames from mechanism M1a. See text for discussion.

same as for the $C_3H_3 + C_3H_3$ reaction. The $C_5H_3 + CH_3$ reactions played a role in the predicted benzene/phenyl formation chemistry, perhaps due to their being only ~32–38 kcal/mol higher in energy than phenyl + H. However, due to concentration effects and a net increase in number of moles, even the $C_2H_2 + i\text{-}C_4H_3$ channel, being 50.8 kcal/mol higher in energy than phenyl + H, was a phenyl decomposition channel in F1. There is a need for clarification of the actual rates and branching ratios of these unsaturated radical-radical combinations that can undergo multiple rearrangements, especially considering some of the possible new pathways presented here.

Consideration of formation pathways of larger aromatic species can be expected to share the same type of effects of the fuel and flame conditions. For example, in the present work, essentially all of the naphthalene formed in F2 and F3 was predicted (from M1a) to be formed by $C_5H_5 + C_5H_5$. In F1, this reaction was second in importance to C_8H_5(o-ethynylphenyl) + $C_2H_2 \Leftrightarrow C_{10}H_7$ (1-naphthyl). Formation of larger PAHs can reasonably be expected to be less strongly affected by falloff behavior, due to the larger molecules' ability to absorb the energy released by chemical activation. It looks as if the most complete answers to questions of the formation of aromatic compounds might never be simple ones.

Acknowledgments

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COMMENTS

K.-H. Homann, TU Darmstadt, Germany. The very early maximum concentration of C_2H, both in acetylene and ethylene flames, could be somehow connected to the formation of benzene that is also a rather early product. Have you any new ideas how C_2H could be formed so early, that is, in the lower-temperature part of the oxidation zone? The traditional path $H + C_2H_2 \rightarrow C_2H + H_2$ is inadequate to explain the early maximum of C_2H.

Author's Reply. In the acetylene flame considered here (Ref. [16] in paper); neither benzene nor C_2H can really be considered an early product, with the peak measured mole fractions occurring well into the reaction zone (at 0.6 and 0.77 cm, respectively), and no significant amount of either before roughly 0.3 and 0.4 cm, respectively. M1a predicts the peak locations well (0.625 and 0.9 cm, respectively). Benzene plays no apparent role (direct or indirect) in C_2H formation. The main formation reaction is $C_2H_2 + OH \leftrightarrow C_2H + H_2O$, which is roughly 5 times more important than $C_2H_2 + H \leftrightarrow C_2H + H_2$. Alternately, in the ethylene flame (Ref. [17] in paper); the measured C_2H peak occurs at 0.83 cm, close to the benzene peak (0.90 cm). While mechanism M1a predicts well the measured C_2H_4, O_2, and C_2H_2 profiles, not only does it predict too early a peak benzene mole fraction (0.45 cm), the peak predicted C_2H mole fraction is too late (1.5 cm). Again,

$C_2H_2 + OH \leftrightarrow C_2H + H_2O$ is the major predicted C_2H formation reaction, but $C_2H_2 + H \leftrightarrow C_2H + H_2$ becomes a net C_2H destruction reaction. The C_4 reactions described above lead to net production of C_2H, becoming more important later in the flame. The possible discrepancies between the data and model for C_2H might therefore reflect limitations in the C_4H_3 chemistry. There is also a predicted contribution to C_2H formation from $C_3H_3 + O \leftrightarrow CH_2O + C_2H$. Since both C_3H_3 and C_4H_3 are relevant to benzene formation, possible significant coupling of the benzene and C_2H chemistry cannot be ruled out.

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Katharina Kohse-Höinghaus, University of Bielefeld, Germany. Does your updated model include NO_x-related chemistry under fuel-rich conditions, or are you considering to include this? It would be very helpful if NO_x reburning chemistry for other fuels than methane could be reliably modeled.

Author's Reply. J. A. Miller has developed a reaction set for describing the C/H/O/N chemistry, which is available from the authors upon request. No changes in the NO_x chemistry resulted from the present work, since this was not a focus of the work, and none of the flames studied in the present work even contain nitrogen.